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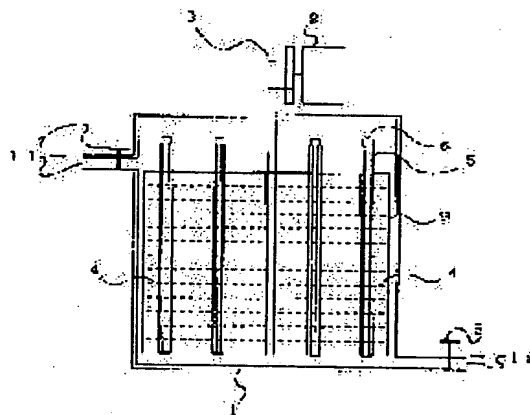
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(54) WATER TREATING DEVICE USING OPTICAL CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a water treating device capable of effectively treating dioxins in water and water to be treated containing organic substances such as endocrine disrupting chemical materials, agricultural chemicals and organic coloring materials by using an optical catalyst.

SOLUTION: A basket frame 9 in which optical catalyst carrying reticulated sheets 4 are horizontally put is installed in a water tank 1 into which the water to be treated flows. The whole of the basket frame 9 is connected to the disk of a motor 2 with a disk by a central shaft 3 to be reciprocated vertically. Black light 6 which is inserted into a glass tube 5 are lit to make the optical catalyst generate hydroxy radicals, and the amount of water coming into contact with the optical catalyst per the unit hour is greatly increased, thereby effectively decomposing the organic substances in the water to be treated at high speed.



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CLAIMS

[Claim(s)]

[Claim 1] Water treatment equipment using the photocatalyst characterized by disassembling the said processed underwater organic substance by irradiating light by said Mitsuteru gunner stage to the reticulated sheet which supported said photocatalyst which is water treatment equipment which disassembles the processed underwater organic substance, and is equipped with the reticulated sheet which supported the photocatalyst, and the Mitsuteru gunner stage which irradiates the light containing ultraviolet rays, and which was immersed in said processed water.

[Claim 2] Photocatalyst water treatment equipment according to claim 1 characterized by making the reticulated sheet which supported said photocatalyst reciprocate by said processed underwater one.

[Claim 3] Water treatment equipment using the photocatalyst according to claim 1 characterized by vibrating the reticulated sheet which supported said photocatalyst by said processed underwater one.

[Claim 4] Water treatment equipment using the photocatalyst according to claim 1 characterized by making it circle in the reticulated sheet which supported said photocatalyst by said processed underwater one.

[Claim 5] Water treatment equipment using the photocatalyst according to claim 1 characterized by making the reticulated sheet which supported said photocatalyst rotate by said processed underwater one.

[Claim 6] Said rotation is water treatment equipment using the photocatalyst according to claim 5 characterized by being what performs forward rotation and counterrotation motion.

[Claim 7] Water treatment equipment using the photocatalyst according to claim 1 to 6 characterized by having a stirring means to agitate said processed water.

[Claim 8] Water treatment equipment using the photocatalyst according to claim 1 to 7 characterized by the light containing said ultraviolet rays being a kind of light chosen from the group which consists of the light of sunlight, a fluorescent lamp, the black light, germicidal lamp glass, a mercury-vapor lamp, a halogen lamp, and an incandescent lamp at least.

[Claim 9] Water treatment equipment using the photocatalyst according to claim 1 to 8 characterized by the thing which is chosen from the group which consists of domestic wasted water, sewage disposal plant wastewater, waste disposal and treatment facility wastewater, paper pulp manufacture facility wastewater, aluminum product manufacture industrial liquid waste, vinyl chloride manufacture industrial liquid waste, an agricultural effluent, golf course wastewater, and coloring wastewater with said processed water, and which is a kind at least.

[Claim 10] Water treatment equipment using the photocatalyst according to claim 1 to 9 characterized by having the control means which controls the inflow blowdown of said processed water to the water treatment equipment using said photocatalyst with said processed underwater organic substance concentration.

[Claim 11] Water treatment equipment using the photocatalyst characterized by disassembling the said processed underwater organic substance by irradiating light by said Mitsuteru gunner stage to the fiber aggregate which supported said photocatalyst which is water treatment equipment which disassembles the processed underwater organic substance, and is equipped with the fiber aggregate which supported the photocatalyst, and the Mitsuteru gunner stage which irradiates the light containing ultraviolet rays, and which was immersed in said processed water.

[Claim 12] Water treatment equipment using the photocatalyst according to claim 11 characterized by the fiber aggregate which supported said photocatalyst being aluminum fiber which supported the photocatalyst.

[Claim 13] It is water treatment equipment which disassembles the processed underwater organic substance, is the sheet-like cloth currently formed by many fibrous objects, and a photocatalyst is supported by the front face of each of said fiber. And each of that fiber It is arranged so that the light irradiated from the exterior can reach to said photocatalyst. And each of that fiber The sheet-like cloth with which mutual physical relationship is arranged so that said processed water can pass with the through put according to the processing object, Water treatment equipment characterized by making said said processed underwater organic substance disassemble in case the sheet-like cloth with which it has the light source which irradiates light to said photocatalyst, and said light is irradiated in said processed water is passed.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the water treatment equipment using a photocatalyst characterized by disassembling the processed underwater organic substance effectively by using a photocatalyst.

[0002]

[Description of the Prior Art] Conventionally, there is a photolysis method which irradiates far ultraviolet rays among the methods of disassembling the organic substance, such as chlorinated organic compounds, such as underwater dioxin. By this approach, dechlorination decomposition is carried out by irradiating the 209-320nm ultraviolet rays which are absorption fields, such as dioxin. However, even if it irradiates and dechlorinates light with a wavelength [of a mercury lamp] of 254nm, between also takes a half-life when and there is a fault with slow catabolic rate. There is the so-called advanced oxidation process (AOP law) which irradiates ultraviolet rays and is decomposed in the approach of on the other hand purifying by carrying out decomposition clearance of the underwater organic substance, adding ozone and a hydrogen peroxide (JP,11-33569,A). This approach has the description with which catabolic rate speeds up as compared with the approach of using only ultraviolet rays. However, it is necessary to supply ozone continuously from an ozonizer, and great energy is needed by the approach of adding ozone underwater. Moreover, by the approach of adding a hydrogen peroxide underwater, the chemical of the hydrogen peroxide solution of a large quantity is needed. Anyway, in this advanced oxidation process, the energy which decomposition takes is large and there is a fault to which water treatment costs become high.

[0003] Furthermore, there is an approach using the water treatment equipment which uses a photocatalyst which seldom needs energy and drugs. According to this approach, energy is seldom needed that what is necessary is just to irradiate a near ultraviolet ray. However, in the water treatment equipment which uses photocatalyst powder (JP,10-202254,A, JP,10-216715,A, JP,10-249336,A, JP,11-151445,A) and a colloid titanium system flocculant (JP,11-188204,A, JP,11-290613,A), although processing effectiveness is high, the film and tub which separate photocatalyst powder are needed.

[0004] Then, bulking agent which supports a photocatalyst (JP,8-47687,A) What supported the photocatalyst to the tub inner surface (JP,10-151450,A), and photocatalyst particle which made it the diameter of 1-3mm using the inorganic system binder (JP,10-202255,A) By the approach by the fixed photocatalyst to be used, separation actuation is not needed. The clarification approach of the pond by the thing of the shape of the discoid which made the photocatalyst support, plate-like, or tubing (JP,11-151486,A) The clarification approach (JP,11-104629,A) is also proposed in water by the raft which made the photocatalyst support. However, in these proposals, since the photocatalyst was supported to the inside of a bulking agent and a tub, the particle, the plate, and the raft, contacting efficiency with water was bad and the technical technical problem that the rate of decomposition was very slow occurred compared with the case where powder is used.

[0005] Furthermore, in addition, the equipment which is made to rotate a disc-like base material and performs raising in processed water after a dipping continuously by things is proposed by JP,10-202257,A. According to this equipment, ultraviolet rays are irradiated in the condition that it was able to pull up from the water surface, and the organic substance by which said disk was adsorbed is disassembled by the photocatalysis. However, with this equipment, only the matter which said disk is easy to adsorb underwater will be disassembled, and the matter by which said disk cannot be adsorbed underwater easily had the technical technical problem that it was not decomposed.

[0006] On the other hand, when a viewpoint is changed to the contamination situation by the organic substance of processed water here, it is in the following situations. That is, dioxin is ***** rare ** to wastewater of a general waste treatment facility and an industrial waste disposal facility. In order to process this raw water, it is carrying out combining the approach of sedimentation, neutralization, aeration, coagulation sedimentation, sand filtration, activated carbon, a filter, and chelate processing. However, since the wastewater which still contained the dioxin of remarkable concentration is discharged, the processing has been a technical problem. Dioxin is contained in high concentration also about wastewater of the paper pulp plant which is a specified facility, an aluminum product plant, and a vinyl chloride plant, and the processing has been a technical problem. For this reason, there is a location where the dioxin exceeding a water standard is detected in public waters.

[0007] Endocrine disrupting chemicals are also detected from public waters. As for bisphenol A which is the raw

material of resin in water quality examination (summer examination 130 point, general autumn water area examination 174 point, and autumn important water area examination 101 point) of the Environment Agency in the Heisei 10 fiscal year, the number of examination points is [the number of detection points of a detection rate] 69% in 255/405, and a detection peak price is 0.94. It was mug/L. The nonyl phenol which is a decomposition product from the raw material of a surfactant is a maximum of 21 in 60% (245/405) of detection rates. mug/L and 4-t-octyl phenol are a maximum of 13 in 56% (228/405) of detection rates. mug/L detection was carried out. The di-2-ethylhexyl phthalate which is the plasticizer of plastics is a maximum of 9.9 in 34% (136/405) of detection rates. mug/L detection was carried out. A maximum of 220 ng/L detection of the polychlorinated biphenyl (PCB) used for a heat carrier, the non carbonic paper, and an electric product was carried out at 69% (281/405) of detection rates. The 17beta-estradiol which is the female sex hormone of the men-and-beasts origin is also a maximum of 0.035 in 64% (260/405) of detection rates. mug/L detection was carried out. Also for the summer Ministry of Construction river dam water quality examination (first-grade river 109 drainage-system 261 point) in the Heisei 11 fiscal year, bisphenol A is a maximum of 0.64 in 44.1% (115/261) of detection rates. mug/L and nonyl phenol are a maximum of 2.0 in 13.4% (35/261) of detection rates. mug/L and 4-t-octyl phenol are a maximum of 0.24 in 9.2% (24/261) of detection rates. mug/L detection was carried out. Di-2-ethylhexyl phthalate is a maximum of 2.4 in 25.3% (66/261) of detection rates. mug/L detection was carried out. 17beta-estradiol is a maximum of 0.0098 in 75.1% (196/261) of detection rates. mug/L detection was carried out.

[0008] In summer examination (the four main sewage disposal plants in Tama River, and the five main sewage disposal plants in Yodogawa) of the inflow sewage of the Ministry of Construction sewerage in the Heisei 11 fiscal year, and a final effluent The percentage reduction which compared the inflow sewage and the final effluent of bisphenol A is 91%→99% (when a final effluent is under a detection lower limit, percentage reduction is computed by the detection lower limit, and writes it as >0%). The median of the percentage reduction computed by median (5th numeric value which is center when measured value of nine examinations is arranged in order with high concentration) g/L of 0.76micro and of inflow sewage, and median g/L of 0.02micro of a sewage effluent is 97%, and a final effluent is a maximum of 0.08. mug/L detection was carried out. For the median of the percentage reduction which the percentage reduction of nonyl phenol is 84%→99%, and was computed by median g/L of 5.6micro and of inflow sewage, and median tr(0.2) mug/L of a final effluent, a final effluent is a maximum of 0.4 at 96%. mug/L. The percentage reduction of di-2-ethylhexyl phthalate is >86%→99%. The median of the percentage reduction computed by median g/L of 4.4micro and of inflow sewage, and median tr(0.2) mug/L of a final effluent is 95%, and is a maximum of 1.9. mug/L detection was carried out (tr beyond a minimum-limit-of-detection value and under a determination limit value). Bisphenol A, nonyl phenol, and di-2-ethylhexyl phthalate have high percentage reduction, and it is considerably removed by sewage treatment. However, the percentage reduction of 17beta-estradiol was 10%→95%, the median of the percentage reduction computed by median g/L of 0.028micro and of inflow sewage, and median g/L of 0.0074micro of a final effluent is 76%, and a maximum of 0.028microg/L detection was carried out. It has been a problem that especially this 17beta-estradiol has low percentage reduction since estrogen activity is high compared with other detected compounds. And it is worried that it may be one of the causes of the abnormalities in a reproductive organ in the carp of the male which inhabits a river. The improvement of the art in the current sewage disposal plant where the activated sludge process has mainly become for the above problem has been a technical problem.

[0009] The ethinylestradiol which is an oral contraceptive has dramatically high female sex hormone activity as well as 17beta-estradiol. Therefore, if the amount used increases, it cannot process from a sewage disposal plant and the amount of the ethinylestradiol discharged in a river will be expected to increase from now on. In order to lose the effect on the living thing which inhabits a river, the decomposition technique of underwater ethinylestradiol is searched for.

[0010] By water quality examination of a river or tap water, without decomposing, the agricultural chemicals used on the paddy field, the field, and the golf course are detected from a river or tap water, and have been problems. The Environment Agency carried out environmental residual surveys, such as agricultural chemicals, as national [urgent] simultaneous examination in the Heisei 10 fiscal year. Consequently, in the water quality examination in July, current was registered as agricultural chemicals and the agricultural chemicals currently suspected to have an endocrine disruption operation were detected. The acetic acid (2, 4-PA) which is the herbicide for paddy fields of a phenoxy system was detected from 37 in the number of 249 examination samples sample, and was maximum-density g/L of 1.56micro. It is detected from 6 in the number of 249 examination samples sample, and is maximum-density g/L of 0.09micro, and the Atrazine which is a triazine herbicide is *****. The simazine (CAT) which is a triazine herbicide was detected from 4 in the number of 249 examination samples sample, and was maximum-density g/L of 0.21micro. The carbaryl (NAC) which is a carver mate system insecticide was detected from 5 in the number of 249 examination samples sample, and was maximum-density g/L of 0.39micro. The meso mill which is a carver mate system insecticide was detected from 10 in the number of 249 examination samples sample, and was maximum-density g/L of 0.30micro. It hydrolyzes in an environment and BENOMIRU which is a carver mate system insecticide remains as carbendazim with teratogenicity. Carbendazim was detected from 16 in the number of 249 examination samples sample, and was maximum-density g/L of 0.3micro. The malathion (marathon) which is an organic phosphorus system insecticide was detected from 3 in the number of 249 examination samples sample, and was maximum-density g/L of 0.32micro. The trifluralin whose alachlor which is the inside of the number of 249 examination samples and an acid-amide system herbicide is a dinitroaniline herbicide in the 3rd examination in November was detected by the concentration of 0.05microg/L from one sample by the concentration of one

sample to 0.38microg/L. In the soil investigation in November, 20microg [/kg] maximum density was carried out for Atrazine, and maximum-density g/kg detection of 6micro of maximum-density g/kg of 77micro, and the malathion was carried out for simazine. Trifluralin is detected from 8 in the number of 48 examination samples sample by the aquatic organism examination in September (fishes), and it is maximum-density g/kg of 4micro, and is *****.

[0011] 0.18microg/L was carried out for acetic acid (2, 4-PA), and tap water examination in June, 2000 was also conducted [simazine] for 0.08microg/L detection of 0.49microg/L and the Atrazine. Consequently, the improvement technique about disassembly of wastewater is searched for about these agricultural chemicals suspected to have the endocrine disruption chemical action for which current is registered into as agricultural chemicals and used on the paddy field, the field, the golf course, etc.

[0012] Compared with a river or the ocean, water pollution is still serious in the lake of closeout nature, a swamp, a landscape pond, and an appreciation pond. Current has the problem of the water pollution by industrial wastewater of a manufacture, agriculture, fisheries, etc., the coloring wastewater containing the organic coloring component of ink or a color, etc. in addition to the endocrine disrupting chemicals, the dioxin, and the agricultural chemicals already explained in full detail.

[0013]

[Problem(s) to be Solved by the Invention] The object of this invention is using a photocatalyst in view of this actual condition, and while it seldom needs energy but holds down water treatment costs low, it is by gathering the effectiveness of contact to processed water and a photocatalyst to offer the water treatment equipment which enables disassembly of the processed underwater organic substance at an early rate.

[0014]

[Means for Solving the Problem] In order to solve an above-mentioned technical problem, as a result of this invention persons' inquiring wholeheartedly, it took notice of the photocatalysis which disassembles the organic substance which exists in processed underwater one that the hydroxy radical generated on the photocatalyst front face reacts with the organic substance, and occurs on a sheet front face. And in order to have raised the decomposition effectiveness of the organic substance, it was solved that it is desirable that it is desirable to consider as the unnecessary fixed photocatalyst of separation instead of powder as for a photocatalyst and to consider as a photocatalyst support reticulated sheet in order to enlarge surface area of a fixed photocatalyst further, that it is desirable to make [many] the amount of the water which, in addition, contacts per unit time amount on a photocatalyst support reticulated sheet front face further, etc.

[0015] Based on this break-through result, the 1st means for solving an above-mentioned technical problem The reticulated sheet which is water treatment equipment which disassembles the processed underwater organic substance, and supported the photocatalyst, It is water treatment equipment using the photocatalyst characterized by disassembling the said processed underwater organic substance by irradiating light by said Mitsuteru gunner stage to the reticulated sheet which supported said photocatalyst equipped with the Mitsuteru gunner stage which irradiates the light containing ultraviolet rays immersed in said processed water.

[0016] The 2nd means is photocatalyst water treatment equipment given in the 1st means characterized by making the reticulated sheet which supported said photocatalyst reciprocate by said processed underwater one.

[0017] The 3rd means is water treatment equipment using a photocatalyst given in the 1st means characterized by vibrating the reticulated sheet which supported said photocatalyst by said processed underwater one.

[0018] The 4th means is water treatment equipment using a photocatalyst given in the 1st means characterized by making it circle in the reticulated sheet which supported said photocatalyst by said processed underwater one.

[0019] The 5th means is water treatment equipment using a photocatalyst given in the 1st means characterized by making the reticulated sheet which supported said photocatalyst rotate by said processed underwater one.

[0020] The 6th means is water treatment equipment using a photocatalyst given in the 5th means characterized by said rotation being what performs forward rotation and counterrotation motion.

[0021] The 7th means is water treatment equipment using a photocatalyst given in either of the 1-6th means characterized by having a stirring means to agitate said processed water.

[0022] The 8th means is water treatment equipment using a photocatalyst given in either of the 1-7th means characterized by the light containing said ultraviolet rays being a kind of light chosen from the group which consists of the light of sunlight, a fluorescent lamp, the black light, germicidal lamp glass, a mercury-vapor lamp, a halogen lamp, and an incandescent lamp at least.

[0023] It is water treatment equipment using a photocatalyst given in either of the 1-8th means characterized by the thing for which the 9th means is chosen from the group to which said processed water changes from domestic wasted water, sewage disposal plant wastewater, waste disposal and treatment facility wastewater, paper pulp manufacture facility wastewater, aluminum product manufacture industrial liquid waste, vinyl chloride manufacture industrial liquid waste, an agricultural effluent, golf course wastewater, and coloring wastewater, and which is a kind at least.

[0024] The 10th means is water treatment equipment using a photocatalyst given in either of the 1-9th means characterized by having the control means which controls the inflow blowdown of said processed water to the water treatment equipment using said photocatalyst with said processed underwater organic substance concentration.

[0025] The fiber aggregate which the 11th means is water treatment equipment which disassembles the processed underwater organic substance, and supported the photocatalyst, It is water treatment equipment using the photocatalyst characterized by disassembling the said processed underwater organic substance by irradiating light

by said Mitsuteru gunner stage to the fiber aggregate which supported said photocatalyst equipped with the Mitsuteru gunner stage which irradiates the light containing ultraviolet rays immersed in said processed water. [0026] The 12th means is water treatment equipment using a photocatalyst given in the 11th means characterized by the fiber aggregate which supported said photocatalyst being aluminum fiber which supported the photocatalyst.

[0027] The 13th means is water treatment equipment which disassembles the processed underwater organic substance. It is the sheet-like cloth currently formed by many fibrous objects, and a photocatalyst is supported by the front face of each of said fiber. And each of that fiber It is arranged so that the light irradiated from the exterior can reach to said photocatalyst. And each of that fiber The sheet-like cloth with which mutual physical relationship is arranged so that said processed water can pass with the through put according to the processing object, In case the sheet-like cloth with which it has the light source which irradiates light to said photocatalyst, and said light is irradiated in said processed water is passed, it is water treatment equipment characterized by making said said processed underwater organic substance disassemble.

[0028]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained, referring to drawing. The vertical reciprocating motion mold water treatment equipment using a photocatalyst which drawing 1 requires for the gestalt of operation of this invention (It is hereafter indicated as both-way mold equipment.) It is vertical reciprocating motion mold water treatment equipment (it is hereafter indicated as round trip mold equipment with a detector.) using the photocatalyst to which it is drawing of longitudinal section and the detector which drawing 2 requires for the gestalt of the operation from which this invention differs was attached. It is stirring mold water treatment equipment (it is hereafter indicated as stirring mold equipment with a detector.) using the photocatalyst to which it is drawing of longitudinal section and the detector which drawing 3 requires for the gestalt of the operation from which this invention differs was attached. It is drawing of longitudinal section, drawing 4 is the cross-sectional view of stirring mold equipment with a detector, and drawing 5 is drawing of longitudinal section of the continuation mold water treatment equipment (it is hereafter indicated as continuation mold equipment.) using a photocatalyst concerning the gestalt of the operation from which this invention differs. In addition, the same sign was attached and shown in the part to which each drawing corresponds.

[0029] Hereafter, the example of a gestalt of operation of this invention is explained based on a drawing. In the both-way mold equipment shown in drawing 1, **** 9 which is fixing the photocatalyst support reticulated sheet 4 mentioned later and the glass tube 5 into which the black light 6 was put is installed in a cistern 1. Furthermore, the **** 9 whole is connected with the disc of the motor 2 with a disc through the main rod 3, and carries out a vertical reciprocating motion by revolution of the motor 2 with a disc. On the other hand, the intake 11 of processed water and the exhaust port 12 of the water after processing are formed in the cistern 1, and the electric ball valves 7 and 8 are installed respectively.

[0030] Here, the following can use it preferably as a photocatalyst support reticulated sheet 4. For example, it is immersed in the emulsion of silicone resin, pull up reticulated glass tissue, and it heats at 290 degrees C. Make a silicone resin layer form on the surface of glass tissue, and the dispersion of polytetrafluoroethylene resin (PTFE) powder is applied on silicone resin. The dispersion of the PTFE powder which heats at 370 degrees C, forms a PTFE layer, and contains a glass bead after that is applied on a PTFE layer. Form the PTFE layer which heats at 370 degrees C and contains a glass bead, and apply the dispersion which contains PTFE powder and an anatase mold photocatalyst titanium oxide particle next on the PTFE layer containing a glass bead, and it is heated at 370 degrees C. a front face — coating weight 20-450g/the photocatalyst titanium oxide particle (mean particle diameter — the range of 0.007-0.5 micrometers —) of m2 the particle size by trade name ST-41 by Ishihara Sangyo Kaisha, Ltd., and this electron microscope of ST-41 — 0.2 micrometers — it is — it is the sheet blanket-like membrane structure material in which the included PTFE layer was made to form. It has been arranged so that the light by which a photocatalyst is supported with performing the above processings by the front face of each fiber, and each of that fiber is irradiated from the exterior can reach to said photocatalyst. As a commercial item, the NITTO DENKO make and fine keeping PFG-SW20H grade can use it preferably.

[0031] The waterproof photocatalyst paper reticulated as a desirable example in which the photocatalyst support reticulated sheets 4 differ may be used. Moreover, in the waterproof paper which a photocatalyst and adsorbents, such as coconut husks activated carbon and permutite, were compound-ized [paper], and made the photocatalyst support in a fiber base material, fabricating is carried out, flexibility is given, and the increase of surface area and the photocatalyst crepe carried out are also desirable. Furthermore, it is also desirable to use photocatalyst corrugated which carried out the laminating of a wave-like photocatalyst sheet and the even photocatalyst sheet one by one, pasted up, and increased the sheet surface area per unit volume.

[0032] It is a configuration also with still more desirable in addition also using the photocatalyst fiber aggregate which gathered the fiber which made the photocatalyst support instead of a photocatalyst support reticulated sheet. As long as it has gathered so that processed water and light may reach each [these] fiber, what kind of configuration is sufficient as this fiber aggregate. If it forms in the shape of [the / as the above-mentioned photocatalyst support reticulated sheet / same] a sheet, the same operation as a photocatalyst support reticulated sheet can be carried out. As fiber which processed water tends to contact, there are aluminum fiber, a glass fiber, a carbon fiber, etc. After making it the shape of yarn after making the front face of these fiber support a photocatalyst, or making it the shape of sponge or making these fiber into the shape of the shape of yarn, or sponge, it is also desirable to use the thing which made the photocatalyst support to a front face. What is

necessary is just to set up suitably the amount of installation of the photocatalyst support reticulated sheet 4 to **** 9 according to conditions, such as a throughput per time amount of processed water, a class of organic substance which should be disassembled, and a content.

[0033] Next, the black light 6 is installed in **** 9, after protecting an outside in glass tube 5 grade. What is necessary is just to also set up the number and wattage of the black light 6 suitably according to conditions, such as a throughput per time amount of processed water, and a class of organic substance which should be disassembled. Here, as the light source which gives light, in addition to the black light 6, it is independent, or sunlight, a fluorescent lamp, germicidal lamp glass, a mercury-vapor lamp, a halogen lamp, an incandescent lamp, etc. can be combined and used to a photocatalyst. What is used as the light source should just choose suitably by the utility of the location in which this water treatment equipment is installed etc. In addition, in explanation of the gestalt of this operation, the thing using the black light 6 as the light source is explained as an example.

[0034] **** 9 in which the photocatalyst support reticulated sheet 4 and the black light 6 were installed as mentioned above performs a vertical reciprocating motion by processed underwater one by the motor 2 with a disc. Here, since the photocatalyst support reticulated sheet 4 is reticulated, the amount of the processed water which contacts unit time amount on photocatalyst support reticulated sheet 4 front face can be made [many] by leaps and bounds, and decomposition effectiveness can be raised. Since it was still more nearly reticulated, there was little resistance of water and it was also able to raise contacting efficiency with processed water with little energy by leaps and bounds.

[0035] Consequently, by having the photocatalyst support reticulated sheet 4 immersed in processed underwater one, and a means to irradiate the light containing ultraviolet rays at the sheet concerned. The hydroxy radical generated by making [many] the amount of the water in contact with a photocatalyst front face, and carrying out UV irradiation to unit time amount to photocatalyst support reticulated sheet 4 front face. It becomes possible to disassemble the chlorinated organic compound and endocrine disrupting chemicals which are the processed underwater organic substance which contacted, agricultural chemicals, the organic coloring matter, etc. at high speed. By furthermore taking this configuration, the photocatalyst support reticulated sheet 4 will receive the exposure of light by processed underwater one, and it will be decomposed by the hydroxy radical generated on the photocatalyst support reticulated sheet 4 even if the photocatalyst support reticulated sheet 4 was hard for the organic substance to adsorb.

[0036] The round trip mold equipment with a detector shown in drawing 2 forms a flow cell 10 and a detector 21 in the both-way mold equipment shown in drawing 1. By taking this configuration, it becomes possible through a detector 21 to control closing motion of the electric ball valve 7 for an inflow, and the electric ball valve 8 for blowdown by measured value of a detector 21 automatically. The processed water of ultralow volume from a cistern 1 with the detector 21 which detects through and organic substance concentration to a flow cell 10 [when decomposition extent of the organic substance is measured, the equipment which controls automatically an inflow in a cistern 1 and the electric ball valves 7 and 8 of blowdown is attached with this decomposition extent and the amount of organic substance of processed water has fluctuation] It becomes [to hold down the organic substance concentration of the processed water discharged from a cistern 1 to below fixed] possible and is desirable.

[0037] the detecting element of a flow cell 10 — for example, the diamond electrode (what formed the conductive diamond polycrystal thin film of a boron dope with the microwave plasma CVD system on the conductive silicon substrate) of high sensitivity — a working electrode and a platinum electrode — a counter electrode and a silver-silver chloride electrode — reference — a pole. By using a linear sweep voltammetry for a detector 21, the current depending on the organic substance concentration between the diamond electrode arranged to the flow cell 10 and a platinum electrode is detectable.

[0038] Although the circle cylindrical basket frame 20 is used for the stirring mold equipment with a detector shown in drawing 3 instead of **** 9 shown in drawing 1 and 2 and it rotates this in a cistern 22 using a motor 23, it is an example. Drawing 4 is the cross-sectional view of this stirring mold equipment with a detector. The glass tube 5 which put the black light 6 into the wall of a cistern 22 in this example, and the photocatalyst support reticulated sheet 4 are fixed, and the photocatalyst support reticulated sheet 4 is further fixed to the circle cylindrical basket frame 20 at a radial. The main rod 3 of the circle cylindrical basket frame 20 is connected with a motor 23, and rotates. In addition, a desirable configuration also makes this revolution the combination of a forward revolution and counterrotation.

[0039] By taking this configuration, it became possible to make [many] the amount of the processed water which contacts unit time amount on a photocatalyst front face in rotation of the photocatalyst support reticulated sheet 4. Since the photocatalyst support reticulated sheet 4 is reticulated, even if it makes it rotate by processed underwater one, there is little resistance of water, and energy required for a revolution has them, and it ends. [few] Moreover, by reversing the photocatalyst reticulated sheet 4 for every predetermined time, it is also possible to gather the effectiveness which contacts a photocatalyst in processed water further as compared with the case where an one direction is rotated, and it is desirable.

[0040] Furthermore, the configuration of the form where the stirring mold equipment with a detector shown in drawing 3 was upset by the request of an installation etc. can also be taken. In that case, a revolving shaft 3 rotates horizontally.

[0041] It is a configuration also with still more desirable in addition in addition to the approach of making the photocatalyst support reticulated sheet 4 exercising, attaching a screw etc. in the pars basilaris ossis occipitalis of

cisterns 1 and 22 etc., rotating this, and also agitating water as a means which makes [more / still] the amount of the processed water which contacts unit time amount on photocatalyst support reticulated sheet 4 front face.

[0042] the continuation mold equipment shown in drawing 5 — telescopic — the glass tube 5 which put the black light 6 into the break and each part store for the column 24 with the dashboard 25 in five rooms is formed, and the photocatalyst support reticulated sheet 4 is arranged in there. telescopic — in order to make processed water flow into a column 24 and to adjust the residence time, the discharge modulating valve 27 is arranged at the inflow modulating valve 26 and the exhaust port 12 at intake 11. telescopic — passage of processed water was lengthened by forming a dashboard 25 in a column 24. It makes it possible to bring forward the rate of flow of the processed water per photocatalyst support reticulated sheet 4 unit cross section by this, and the catabolic rate of the organic substance is raised. In this configuration, the rate of flow of processed water can be used further, the quantity of water to be treated — which is going and coming back to the photocatalyst support reticulated sheet 4, vibrating, and making it circle, and touches a photocatalyst can also be made to increase further, and it is desirable.

[0043] As mentioned above, if the water treatment equipment using the photocatalyst concerning the gestalt of operation of this invention explained in full detail is installed in the culmination of the waste water treatment of a domestic-wastes incineration facility, an industrial-waste-incineration facility, paper pulp manufacture facility wastewater and aluminum product manufacture industrial liquid waste, and vinyl chloride manufacture industrial liquid waste, it can perform easily lowering even to the concentration of 10 or less pg-TEQ/L of the emission standard of dioxin. moreover, if this water treatment equipment is installed in the phase of the final treatment of a sewage disposal plant, the elimination factor of 17beta-estradiol or ethinylestradiol can also be boiled markedly, and can improve, the concentration of the 17beta-estradiol in a river or ethinylestradiol can decrease, and the abnormalities of the carp which inhabits a river can be improved. Furthermore, if this water treatment equipment is installed in the drainage system of agriculture or a golf course, the agricultural chemicals (acetic acid (2, 4-PA), Atrazine, simazine (CAT), carbaryl (NAC), a meso mill, BENOMIRU, a malathion (marathon), alachlor, trifluralin) currently suspected to have endocrine disruption chemical action can be lowered to the concentration below the provisional instruction guide concerning the water quality assessment guide and golf course activity agricultural chemicals in public waters etc. Decolorization of wastewater can also be made easy if this water treatment equipment is furthermore installed in the drainage system containing the organic coloring component of coloring ink or a color in addition.

[0044] (Example 1) The both-way mold equipment shown in drawing 1 was used. As a cistern 1, 950mm long, 950mm wide, and a square shape cistern with a height of 1400mm were used. 100 sheets (with a width-of-face die length [900mm die length of 900mm] size) were fixed to **** (900mm long, side of 900mm, height of 1000mm) 9 at a level with 10mm spacing, using "coating weight 115 g/m² to the shape of 0.30mm in the NITTO DENKO make, fine keeping PFG-SW20H, and thickness, the thread width of 0.5mm, eye vacancy width of face of 1mm, and a grid, 49% of hole density, and a photocatalyst titanium oxide particle front face" as a photocatalyst support reticulated sheet 4. Next, the glass tube 5 into which the 40W black light 6 with a die length of 1198mm was put was fixed to the vertical by 16 regular intervals at **** 9.

[0045] And closing and the electric ball valve 7 for an inflow were opened for the electric ball valve 8 for blowdown of a cistern 1, and the water of 0.90m³ which contained 2,4-dichlorophenol 90microg/L (5.5×10^{-7} mol/L) as model matter of dioxin was put in to a depth of 1000mm. The 16 black lights 6 were turned on here and the **** 9 whole was made for single phase and the motor 2 with a disc of 100V and 200W to move up and down 40mm with the main rod 3 with the speed of 60rpm. Then, 2,4-dichlorophenol becomes 9.0microg/L (1/10 of initial concentration) in 15 minutes after a start up, and it is ***** to 0.90microg/L (1/100 of initial concentration) in 30 minutes. Then, 30 minutes after dropping to 1/100 of initial concentration, the electric ball valve 8 for blowdown was opened, and the processed water of a cistern 1 was discharged. After shutting the electric ball valve 8 for blowdown, the electric ball valve 7 for an inflow was opened, the water which should be processed again was put in to a depth of 900mm, and equipment was operated. When this equipment was operated in this cycle on the 1st, the organic substance of the processed water of 3 was able to be processed or less [of initial concentration] to 1/100 43m.

[0046] (Example 2) This equipment was operated on the same conditions as an example 1 except having changed 2,4-dichlorophenol 90microg/L (5.5×10^{-7} mol/L) to 17beta-estradiol 90microg/L (3.3×10^{-7} mol/L) as the organic substance which should decompose processed underwater one. Then, 17beta-estradiol became 9.0microg/L (1/10 of initial concentration) in 6 minutes, and became 0.90microg/L (1/100 of initial concentration) in 12 minutes.

[0047] (Example 3) This equipment was operated on the same conditions as an example 1 except having changed 2,4-dichlorophenol 90microg/L (5.5×10^{-7} mol/L) as the organic substance which should decompose processed underwater one to sodium salt 1.0 mg/L (4.5×10^{-6} mol/L) of the acetic acid (2, 4-PA) which is a herbicide for paddy fields. Then, acetic acid became 0.10 mg/L (1/10 of initial concentration) in 10 minutes, and became 0.010 mg/L (1/100 of initial concentration) in 20 minutes.

[0048] (Example 4) This equipment was operated on the same conditions as an example 1 except having changed 2,4-dichlorophenol 90microg/L (5.5×10^{-7} mol/L) to coloring color methylene-blue water-solution 10 mg/L as the organic substance which should decompose processed underwater one. Then, the methylene blue became 1.0 mg/L (1/10 of initial concentration) in 15 minutes, and became 0.10 mg/L (1/100 of initial concentration) in 30 minutes, and the solution became transparence.

[0049] (Example 5) This equipment was operated on the same conditions as an example 1 as the organic substance which should decompose processed underwater one except having changed 2,4-dichlorophenol 90microg/L

(5.5×10^{-7} mol/L) to coloring color eosine Y water-solution 20 mg/L. Then, eosine Y became 2.0 mg/L (1/10 of initial concentration) in 15 minutes, and became 0.20 mg/L (1/100 of initial concentration) in 30 minutes, and the solution became transperence.

[0050] (Example 6) This using the round trip mold equipment with a detector shown in drawing 2 installs a flow cell 10 and a detector 21 in the equipment of an example 1. In the flow cell 10 interior, the operation pole has been arranged for the diamond electrode (what formed the conductive diamond polycrystal thin film of a boron dope with the microwave plasma CVD system on the conductive silicon substrate) of high sensitivity, and the counter electrode and the silver-silver chloride electrode have been arranged for the platinum electrode as a reference pole. The linear sweep voltammetry was used as a detector 21. 90micro g/L (3.9×10^{-7} mol/L) of bisphenol A was used as the organic substance which should decompose processed underwater one.

[0051] The water of a cistern 1 was first incorporated to the flow cell 10 continuously, and the phosphate buffer solution of pH7.2 was added as a supporting electrolyte. 4.0nA(s) were shown, when the rate of flow of a flow cell 10 was made into 1 mL/min, potential of the diamond electrode of high sensitivity was set to +0.75V and the current value was measured. When the vertical reciprocating motion of the photocatalyst support reticulated sheet 4 was carried out like the example 1, the light of the black light 6 was irradiated and for 10 minutes was operated, potential +0.75V showed current value 0.40nA, and it turned out that bisphenol A became 1/10 of 9.0microg/L of initial concentration. When the vertical reciprocating motion of the photocatalyst support reticulated sheet 4 was carried out, the light of the black light 6 was irradiated and equipment was operated for 20 minutes, potential +0.75V showed current value 0.04nA, and it became clear that bisphenol A became 1/100 of 0.9microg/L of initial concentration.

[0052] (Example 7) The processor was operated like the example 6 except having changed 90micro g/L (3.9×10^{-7} mol/L) of bisphenol A to carbaryl (NAC) 1.0 mg/L (5.0×10^{-6} mol/L) which is agricultural chemicals as the organic substance which should decompose processed underwater one. The water of a cistern 1 was continuously incorporated to the flow cell 10, and the phosphate buffer solution of pH7.2 was added as a supporting electrolyte. 100nA(s) were shown, when the rate of flow of a flow cell 10 was made into 1 mL/min, potential of the diamond electrode of high sensitivity was set to +1.4V and the current value was measured. When the vertical reciprocating motion of the photocatalyst support reticulated sheet 4 was carried out, the light of the black light 6 was irradiated and for 10 minutes was operated, potential +1.4V showed current value 10nA, and it turned out that carbaryl became 1/10 of 0.1 mg/L of initial concentration. When the vertical reciprocating motion of the photocatalyst support reticulated sheet 4 was carried out, the light of the black light 6 was irradiated and for 20 minutes was operated, potential +1.4V showed current value 1.0nA, and it became clear that carbaryl became 1/100 of 0.01 mg/L of initial concentration.

[0053] (Example 8) The churning mold equipment with a detector shown in drawing 3 was used. The glass tube 5 which put the 40W black light 6 with a die length of 1198mm into the cylindrical cistern 22 with a diameter [of 900mm] and a height of 1050mm was fixed to the wall of a cistern at 8 regular intervals. "As the photocatalyst support reticulated sheet 4 The NITTO DENKO make, fine keeping PFG-SW20H, The shape of 0.30mm in thickness, the thread width of 0.5mm, eye vacancy width of face of 1mm, and a grid, 49% of hole density. This cross section that attached the photocatalyst support reticulated sheet 4 of a with a width-of-face die length [1m die length of 320mm] size in the circle cylindrical basket frame 20 with a die length of 320mm which came out to the perimeter of 32 sheets and the main rod 3 at the radial is shown in drawing 4 using coating weight 115 g/m² to a photocatalyst titanium oxide particle front face." As furthermore shown in drawing 4, the photocatalyst support reticulated sheet 4 of a with a width-of-face die length [1m die length of 6mm] size was fixed to the wall of a cistern 22 at 32-sheet regular intervals.

[0054] And the processed water of 0.56m³ which opened closing and the electric ball valve 7 for an inflow for the electric ball valve 8 for blowdown of a cistern 22, and contained 90micro g/L (3.9×10^{-7} mol/L) of bisphenol A as the processed underwater organic substance which should decompose was put in to a depth of 900mm. The eight black lights 6 are turned on, and make it rotate for 15 seconds with the speed of 60rpm; it was made to stop for 5 seconds, the main rod 3 was reversed for 15 seconds, and it was made to stop for 5 seconds by single phase, 100V, and 200W motor 23 here. It carried out by having repeated this actuation and processed water was agitated.

[0055] The rate of flow was continuously incorporated for the water of the cylinder cistern 22 to the flow cell 10 which made the operation pole and the platinum electrode the counter electrode, and has, on the other hand, arranged the diamond electrode (what formed the conductive diamond polycrystal thin film of a boron dope with the microwave plasma CVD system on the conductive silicon substrate) of high sensitivity inside by making a silver-silver chloride electrode into a reference pole by 1 mL/min, and the phosphate buffer solution of pH7.2 was added to it as a supporting electrolyte. 4.0nA(s) were shown, when potential of the linear sweep voltammetry of a detector 21 was set to +0.75V and the current value was measured. Then, when the light of the black light 6 was irradiated and for 20 minutes was operated, having reversed the photocatalyst support reticulated sheet 4 and agitating water, potential +0.75V showed current value 0.40nA, and it became clear that bisphenol A became 1/10 of 9.0microg/L of initial concentration.

[0056] Furthermore, when the light of the black light 6 was irradiated and equipment was operated for 40 minutes, agitating, potential +0.75V showed current value 0.04nA, and it became clear that bisphenol A became 0.9microg/L which is 1/100 of initial concentration. And after [of a start up] 40 minutes which dropped to 1/100 of initial concentration, the electric ball valve 8 for blowdown was opened, and the treated water of the cylinder cistern 22 was discharged. Next, after shutting the electric ball valve 8 for blowdown, the electric ball valve 7 for an inflow

was opened, the water which should be processed again was put in to a depth of 900mm, and equipment was operated. When this equipment was operated in this cycle on the 1st, the organic substance of the processed water of 3 was able to be processed or less [of initial concentration] to 1/100 20m.

[0057] (Example 9) The continuation mold equipment shown in drawing 5 was used. telescopic — inside the column 24 (it is bore 0.95mx0.95m at height of 2.5m), by 0.95mx0.90m, as shown in drawing 5, a break and passage were set to 5.4m for the dashboard 25 with a thickness of 4mm in four-sheet installation and five rooms at 0.5m interval. The glass tube into which the 40W black light 6 with a die length of 1198mm was put was detached 0.5m to each other, and it attached two in each part store at a time a total of ten. 90 things which made the photocatalyst support reticulated sheet 4 "coating weight 115. g/m² to the shape of 0.30mm in the NITTO DENKO make, fine keeping PFG-SW20H, and thickness, the thread width of 0.5mm, eye vacancy width of face of 1mm, and a grid, 49% of hole density, and a photocatalyst titanium oxide particle front face" 0.95mx0.42m size were arranged in each part store at right angles to 10mm spacing.

[0058] the processed water which contained 17beta-estradiol 90microg/L (3.3×10^{-7} mol/L) as the organic substance which should decompose processed underwater one is set to 0.038m³/min of the rates of flow — as — the inflow modulating valve 26 — adjusting — telescopic — it was made to flow into a column 24 continuously, the discharge modulating valve 27 was adjusted so that the residence time might become for 80 minutes, and the black light 6 was turned on. then, telescopic — the processed underwater 17beta-estradiol which flows out from a column 9 became 0.90microg/L (1/100 of initial concentration). When this equipment was operated by this rate of flow on the 1st, it became clear that the processed underwater 17beta-estradiol of 3 could be processed or less [of inflow concentration] to 1/100.55m.

[0059]

[Effect of the Invention] The reticulated sheet which is water treatment equipment which disassembles the processed underwater organic substance in this invention, and supported the photocatalyst as explained in full detail above, It had the Mitsuteru gunner stage which irradiates the light containing ultraviolet rays, and the water treatment equipment using the photocatalyst characterized by disassembling the said processed underwater organic substance by irradiating light by said Mitsuteru gunner stage to the reticulated sheet which supported said photocatalyst immersed in said processed water was invented. While energy was seldom needed but water treatment costs were low held down by using this water treatment equipment, it became possible by gathering the effectiveness of contact to processed water and a photocatalyst to disassemble the processed underwater organic substance at an early rate.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing of longitudinal section of the both-way mold equipment concerning the gestalt of operation of this invention.

[Drawing 2] It is drawing of longitudinal section of the round trip mold equipment with a detector concerning the gestalt of operation of this invention.

[Drawing 3] It is drawing of longitudinal section of the churning mold equipment with a detector concerning the gestalt of operation of this invention.

[Drawing 4] It is the cross-sectional view of the churning mold equipment with a detector concerning the gestalt of operation of this invention.

[Drawing 5] It is drawing of longitudinal section of the continuation mold equipment concerning the gestalt of operation of this invention.

[Description of Notations]

1. a cistern, a motor with 2. disc, 3. core rod, 4. photocatalyst support reticulated sheet, 5. glass tube, 6. black light, the electric ball valve for 7. inflow, the electric ball valve for 8. blowdown, 9. ****, 10. flow cell, 11. intake, 12. exhaust port, 20. circle cylindrical basket frame, 21. detector, 22. cistern, 23. motor, and 24. telescopic — a column, 25. dashboard, 26. inflow modulating valve, and 27. discharge modulating valve.

[Translation done.]

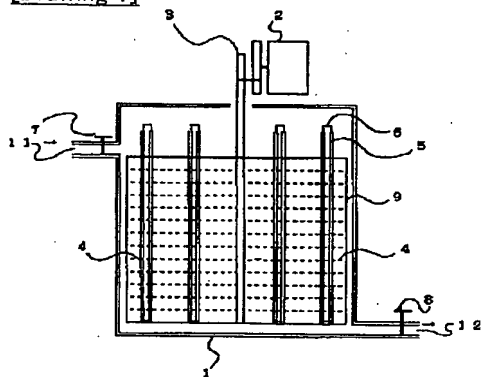
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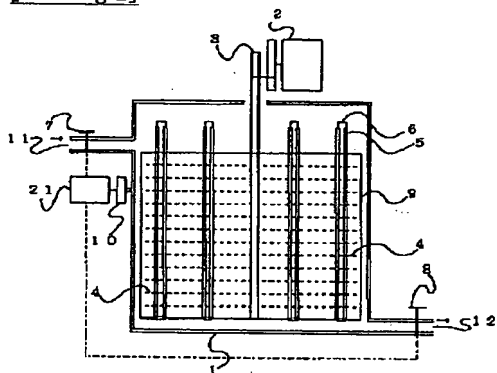
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DRAWINGS

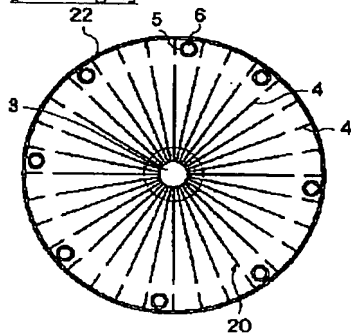
[Drawing 1]



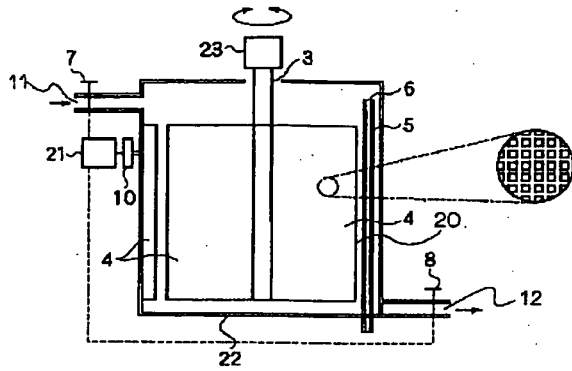
[Drawing 2]



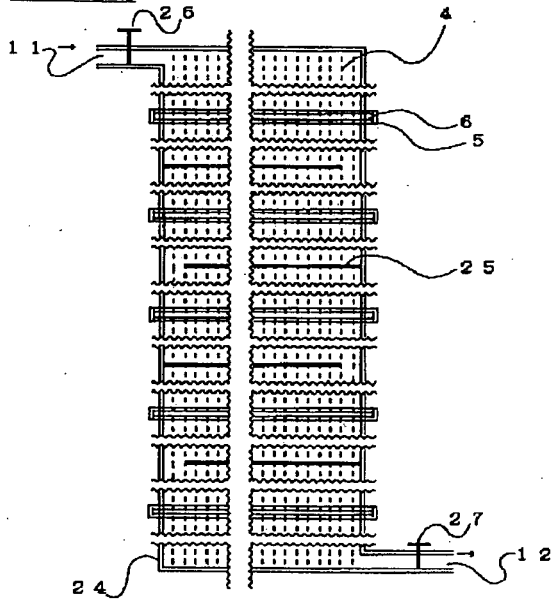
[Drawing 4]



[Drawing 3]



[Drawing 5]



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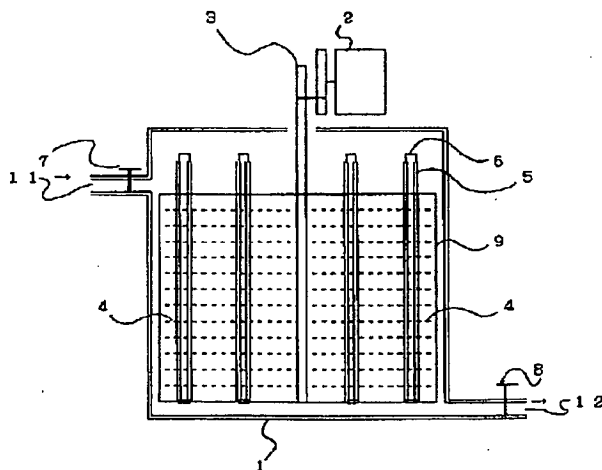
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(54) 【発明の名称】 光触媒を用いた水処理装置

(57) 【要約】

【課題】 光触媒を用いて水中のダイオキシン類や内分泌攪乱化学物質、農薬、有機着色物質等の有機物を含む被処理水を効率よく処理する水処理装置を提供する。

【解決手段】 被処理水を流入させる水槽1内に、光触媒担持網状シート4を水平に張った籠枠9を設置する。そして籠枠9全体を中心軸3により円盤付きモーター2の円盤へ連結して、上下往復運動させる。そしてガラス管5に入れたブラックライト6を点灯して光触媒にヒドロキシラジカルを発生させる一方、単位時間に光触媒に接する水の量を飛躍的に増やすことで、被処理水中の有機物を高速で且つ効率良く分解する。



【特許請求の範囲】

【請求項1】 被処理水中の有機物を分解する水処理装置であって、

光触媒を担持した網状シートと、紫外線を含有する光を照射する光照射手段とを備え、

前記被処理水に浸漬された前記光触媒を担持した網状シートへ、前記光照射手段により光を照射することで、前記被処理水中の有機物を分解することを特徴とする光触媒を用いた水処理装置。

【請求項2】 前記光触媒を担持した網状シートを、前記被処理水中で往復運動させることを特徴とする請求項1記載の光触媒水処理装置。

【請求項3】 前記光触媒を担持した網状シートを、前記被処理水中で振動させることを特徴とする請求項1記載の光触媒を用いた水処理装置。

【請求項4】 前記光触媒を担持した網状シートを、前記被処理水中で旋回運動させることを特徴とする請求項1記載の光触媒を用いた水処理装置。

【請求項5】 前記光触媒を担持した網状シートを、前記被処理水中で回転運動させることを特徴とする請求項1記載の光触媒を用いた水処理装置。

【請求項6】 前記回転運動とは正回転運動と逆回転運動とを行なうものであることを特徴とする請求項5記載の光触媒を用いた水処理装置。

【請求項7】 前記被処理水を攪拌する攪拌手段を有することを特徴とする請求項1～6のいずれかに記載の光触媒を用いた水処理装置。

【請求項8】 前記紫外線を含有する光とは、太陽光、蛍光灯、ブラックライト、殺菌灯、水銀灯、ハロゲンランプ及び白熱ランプの光より成る群から選ばれる少なくとも一種の光であることを特徴とする請求項1～7のいずれかに記載の光触媒を用いた水処理装置。

【請求項9】 前記被処理水とは、生活排水、下水処理場排水、廃棄物処理施設排水、紙パルプ製造施設排水、アルミニウム製品製造工場排水、塩化ビニル製造工場排水、農業排水、ゴルフ場排水、着色排水より成る群から選ばれる少なくとも一種であることを特徴とする請求項1～8のいずれかに記載の光触媒を用いた水処理装置。

【請求項10】 前記被処理水中の有機物濃度により、前記光触媒を用いた水処理装置への、前記被処理水の流入排出を制御する制御手段を有することを特徴とする請求項1～9のいずれかに記載の光触媒を用いた水処理装置。

【請求項11】 被処理水中の有機物を分解する水処理装置であって、

光触媒を担持した繊維集合体と、紫外線を含有する光を照射する光照射手段とを備え、

前記被処理水に浸漬された前記光触媒を担持した繊維集合体へ、前記光照射手段により光を照射することで、前記被処理水中の有機物を分解することを特徴とする光触

媒を用いた水処理装置。

【請求項12】 前記光触媒を担持した繊維集合体が、光触媒を担持したアルミニウム繊維であることを特徴とする請求項11記載の光触媒を用いた水処理装置。

【請求項13】 被処理水中の有機物を分解する水処理装置であって、

多数の繊維状物にて形成されているシート状布であって、前記各繊維の表面には光触媒が担持され、且つ、その各繊維は、外部より照射される光が前記光触媒へ到達できるように配置されたものであり、且つ、その各繊維は、前記被処理水が処理目的に応じた通過量で通過できるように、互いの位置関係が配置されたものであるシート状布と、

前記光触媒へ光を照射する光源とを有し、

前記被処理水を前記光が照射されているシート状布を通過させる際に、前記被処理水中の前記有機物を分解させることを特徴とする水処理装置。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、被処理水中の有機物を、光触媒を用いることで効果的に分解することを特徴とする、光触媒を用いた水処理装置に関する。

【0002】

【従来の技術】従来、水中のダイオキシン類などの有機塩素系化合物等の有機物の分解法には、遠紫外線を照射する光分解法がある。この方法では、ダイオキシン類などの吸収領域である209～320nmの紫外線を照射することにより、脱塩素分解される。しかし水銀ランプの波長254nmの光を照射して、脱塩素化しても、半減期が何時間もかかり、分解速度が遅い欠点がある。一方、水中の有機物を分解除去することにより浄化する方法には、オゾンや過酸化水素を添加しながら、紫外線を照射して分解する、いわゆる促進酸化法(AOP法)がある(特開平11-33569)。この方法は紫外線のみを用いる方法と比較して、分解速度が速まる特徴がある。しかし、オゾンを水中に添加する方法では、オゾン発生機から絶えずオゾンを供給する必要があり、多大なエネルギーを必要とする。また過酸化水素を水中に添加する方法では、大量の過酸化水素水の薬品が必要になる。いずれにしても、この促進酸化法では、分解に要するエネルギーが大きく、水処理費用が高くなる欠点がある。

【0003】さらに、エネルギーや薬剤をあまり必要としない、光触媒を使用する水処理装置を用いる方法がある。この方法によれば近紫外線を照射するだけでよく、エネルギーをあまり必要としない。しかし光触媒粉末

(特開平10-202254、特開平10-216715、特開平10-249336、特開平11-151445)やコロイド状チタン系凝集剤(特開平11-188204、特開平11-290613)を使用する水処理装置においては、処理効率は高いものの光触媒粉末を分離する膜や槽が必要になる。

【0004】そこで、光触媒を担持する充填剤（特開平8-47687）、光触媒を槽内面に担持したもの（特開平10-151450）、無機系バインダーを用いて直径1～3mmにした光触媒粒子（特開平10-202255）を使用する固定化光触媒による方法では分離操作がいらぬ。光触媒を担持させた円盤状、平板状または管状のものによる池の浄化方法（特開平11-151486）や光触媒を担持させた筏により水を浄化方法（特開平11-104629）も提案されている。ところがこれらの提案においては、光触媒を充填剤・槽内・粒子・板・筏に担持しているために、水との接触効率が悪く、粉末を使用する場合と比べ、分解の速度が大変遅いという技術的課題があった。

【0005】さらに加えて、特開平10-202257には、円板状支持体を回転させことで連続的に被処理水に浸せき後、引き上げをおこなう装置が提案されている。この装置によれば、前記円板に吸着された有機物は水面から引き上げられた状態で紫外線が照射され、光触媒反応により分解される。しかしながら、この装置では水中で前記円板に吸着されやすい物質のみ分解されることになり、水中で前記円板に吸着されにくい物質は分解されないという技術的課題があった。

【0006】一方、ここで観点を被処理水の有機物による汚染状況に転じてみると、以下のような状況である。すなわち、ダイオキシン類が一般廃棄物処理施設及び産業廃棄物処理施設の排水に高濃度含まれる。この原水を処理するために、沈降、中和、曝気、凝集沈殿、砂ろ過、活性炭、フィルター、キレート処理の方法を組み合わせで行っている。しかし、まだかなりの濃度のダイオキシン類を含んだ排水を放流しているため、その処理が課題になっている。特定施設である紙パルプ製造工場、アルミニウム製品製造工場、塩化ビニル製造工場の排水についてもダイオキシン類が高濃度に含まれ、その処理が課題になっている。このため、公共用水域で、水質基準を上回るダイオキシン類が検出されている場所がある。

【0007】内分泌攪乱化学物質も公共用水域から検出されている。平成10年度環境庁の水質調査（夏季調査130地点と秋季一般水域調査174地点と秋季重点水域調査101地点）では、樹脂の原料であるビスフェノールAは調査地点数が405で検出地点数が255で検出割合は69%であり、検出最高値は0.94 $\mu\text{g/L}$ であった。界面活性剤の原料で分解生成物であるノニルフェノールが検出割合60%（245/405）で最高21 $\mu\text{g/L}$ 、4-t-オクチルフェノールは検出割合56%（228/405）で最高13 $\mu\text{g/L}$ 検出された。プラスチックの可塑剤であるフタル酸ジ-2-エチルヘキシルは検出割合34%（136/405）で最高9.9 $\mu\text{g/L}$ 検出された。熱媒体、ノンカーボン紙、電気製品に用いられるポリ塩化ビフェニール類（PCB）は検出割合69%（281/405）で最高220 ng/L検出された。人畜由来の

女性ホルモンである17 β -エストラジオールも検出割合64%（260/405）で最高0.035 $\mu\text{g/L}$ 検出された。平成11年度夏期建設省河川ダム水質調査（一級河川109水系261地点）でもビスフェノールAが検出割合44.1%（115/261）で最高0.64 $\mu\text{g/L}$ 、ノニルフェノールが検出割合13.4%（35/261）で最高2.0 $\mu\text{g/L}$ 、4-t-オクチルフェノールは検出割合9.2%（24/261）で最高0.24 $\mu\text{g/L}$ 検出された。フタル酸ジ-2-エチルヘキシルは検出割合25.3%（66/261）で最高2.4 $\mu\text{g/L}$ 検出された。17 β -エストラジオールは検出割合75.1%（196/261）で最高0.0098 $\mu\text{g/L}$ 検出された。

【0008】平成11年度建設省下水道の流入下水と放流水の夏期調査（多摩川の主な下水処理場4ヶ所と淀川の主な下水処理場5ヶ所）では、ビスフェノールAの流入下水と放流水を比較した減少率は91%～>99%（放流水が検出下限値未満の場合、減少率は検出下限値で算出し>〇%と表記）で、流入下水の中央値（調査9ヶ所の測定値を濃度の高い順に並べた時に中央である5番目の数値）0.76 $\mu\text{g/L}$ 及び放流水の中央値0.02 $\mu\text{g/L}$ で算出した減少率の中央値は97%で、放流水は最高0.08 $\mu\text{g/L}$ 検出された。ノニルフェノールの減少率は84%～>99%で、流入下水の中央値5.6 $\mu\text{g/L}$ 及び放流水の中央値tr（0.2） $\mu\text{g/L}$ で算出した減少率の中央値は96%で放流水は最高0.4 $\mu\text{g/L}$ 、フタル酸ジ-2-エチルヘキシルの減少率は>86%～>99%で、流入下水の中央値4.4 $\mu\text{g/L}$ 及び放流水の中央値tr（0.2） $\mu\text{g/L}$ で算出した減少率の中央値は95%で、最高1.9 $\mu\text{g/L}$ 検出された（trとは検出下限値以上かつ定量下限値未満）。ビスフェノールA、ノニルフェノール、フタル酸ジ-2-エチルヘキシルは、減少率が高く、下水処理でかなり除去されている。しかし、17 β -エストラジオールの減少率は10%～>95%で、流入下水の中央値0.028 $\mu\text{g/L}$ 及び放流水の中央値0.0074 $\mu\text{g/L}$ で算出した減少率の中央値は76%で、最高0.028 $\mu\text{g/L}$ 検出された。特に、この17 β -エストラジオールは検出された他の化合物と比べてエストロゲン活性が高いために、減少率が低いことが問題になっている。そして、河川に棲息する雄の鯉における生殖器異常の原因の一つではないかと心配されているものである。以上の問題のために、活性汚泥法が主になっている現在の下水処理場での処理方法の改善が課題になっている。

【0009】経口避妊薬であるエチニルエストラジオールは、女性ホルモン活性が17 β -エストラジオールと同じく非常に高い。そのため、使用量が増加すれば、下水処理場から処理できなくて、河川へ排出されるエチニルエストラジオールの量が、今後多くなると予想される。河川に棲息する生物への影響をなくするため、水中のエチニルエストラジオールの分解技術が求められている。

【0010】河川や水道水の水質調査で、水田や畑、ゴルフ場で使用された農薬が、分解せずに、河川や水道水から検出され問題になっている。環境庁は平成10年度緊急全国一斉調査として、農薬等の環境残留実態調査を実施した。その結果、7月の水質調査では、現在も農薬として登録され、内分泌攪乱作用を有すると疑われている農薬が検出された。フェノキシ系の水田用除草剤である2, 4-ジクロロフェノキシ酢酸(2, 4-P A)は、249調査試料数中37試料から検出され、最高濃度1. 56 $\mu\text{g/L}$ であった。トリアジン系除草剤であるアトラジンは、249調査試料数中6試料から検出され、最高濃度0. 09 $\mu\text{g/L}$ であった。トリアジン系除草剤であるシマジン(C A T)は249調査試料数中4試料から検出され、最高濃度0. 21 $\mu\text{g/L}$ であった。カーバメイト系殺虫剤であるカルバリル(N A C)は、249調査試料数中5試料から検出され、最高濃度0. 39 $\mu\text{g/L}$ であった。カーバメイト系殺虫剤であるメソミルは249調査試料数中10試料から検出され、最高濃度0. 30 $\mu\text{g/L}$ であった。カーバメイト系殺虫剤であるベノミルは、環境中で加水分解され、催奇形性のあるカルベンダジムとして残留する。カルベンダジムは249調査試料数中16試料から検出され、最高濃度0. 3 $\mu\text{g/L}$ であった。有機リン系殺虫剤であるマラチオン(マラソン)は、249調査試料数中3試料から検出され、最高濃度0. 32 $\mu\text{g/L}$ であった。11月の第3回調査で249調査試料数中、酸アミド系除草剤であるアラクロールが、1試料から0. 38 $\mu\text{g/L}$ の濃度で、ジネトロアニリン系除草剤であるトリフルラリンが1試料から、0. 05 $\mu\text{g/L}$ の濃度で検出された。11月の土壌調査ではアトラジンが最高濃度20 $\mu\text{g/kg}$ 、シマジンが最高濃度77 $\mu\text{g/kg}$ 、マラチオンが最高濃度6 $\mu\text{g/kg}$ 検出された。9月の水生生物調査(魚類)でトリフルラリンが48調査試料数中8試料から検出され、最高濃度4 $\mu\text{g/kg}$ であった。

【0011】2000年6月の水道水調査でも、2, 4-ジクロロフェノキシ酢酸(2, 4-P A)が0. 18 $\mu\text{g/L}$ 、シマジンが0. 49 $\mu\text{g/L}$ 、アトラジンが0. 08 $\mu\text{g/L}$ 検出された。この結果、現在も農薬として登録され、水田・畑・ゴルフ場等で使用されている、内分泌攪乱化学作用を有すると疑われるこれらの農薬については、排水の分解に関する改善技術が求められている。

【0012】閉鎖性の湖、沼、修景池、鑑賞池などでは、河川や海洋と比べ、依然として、水汚染が深刻である。すでに詳述した、内分泌攪乱化学物質・ダイオキシン類・農薬以外に、現在でも、製造業、農業、水産業などの産業排水、インクや染料の有機着色成分を含む着色排水などによる水汚染の問題がある。

【0013】

【発明が解決しようとする課題】本発明の目的は、かかる現状に鑑み、光触媒を用いることで、エネルギーをあまり必要とせず水処理費用を低く抑える一方、被処理水と光触媒との接触の効率を上げることにより、被処理水中における有機物の分解を早い速度で可能とする水処理装置を提供することにある。

【0014】

【課題を解決するための手段】上述の課題を解決するために本発明者らが鋭意研究した結果、被処理水中に存在する有機物を分解する光触媒反応は、光触媒表面で生成したヒドロキシラジカルがシート表面で有機物と反応して起きることに注目した。そして有機物の分解効率を向上させるには、光触媒は粉末ではなく分離の不必要な固定化光触媒とすることが好ましいこと、さらに固定化光触媒の表面積を大きくするために光触媒担持網状シートとすることが好ましいこと、さらに加えて単位時間当たりに光触媒担持網状シート表面に接触する水の量を多くすることが好ましいこと、等が解明された。

【0015】この解明結果に基づき、上述の課題を解決するための第1の手段は、被処理水中の有機物を分解する水処理装置であって、光触媒を担持した網状シートと、紫外線を含有する光を照射する光照射手段とを備え、前記被処理水に浸漬された前記光触媒を担持した網状シートへ、前記光照射手段により光を照射することで、前記被処理水中の有機物を分解することを特徴とする光触媒を用いた水処理装置である。

【0016】第2の手段は、前記光触媒を担持した網状シートを、前記被処理水中で往復運動させることを特徴とする第1の手段に記載の光触媒水処理装置である。

【0017】第3の手段は、前記光触媒を担持した網状シートを、前記被処理水中で振動させることを特徴とする第1の手段に記載の光触媒を用いた水処理装置である。

【0018】第4の手段は、前記光触媒を担持した網状シートを、前記被処理水中で旋回運動させることを特徴とする第1の手段に記載の光触媒を用いた水処理装置である。

【0019】第5の手段は、前記光触媒を担持した網状シートを、前記被処理水中で回転運動させることを特徴とする第1の手段に記載の光触媒を用いた水処理装置である。

【0020】第6の手段は、前記回転運動とは正回転運動と逆回転運動とを行なうものであることを特徴とする第5の手段に記載の光触媒を用いた水処理装置である。

【0021】第7の手段は、前記被処理水を攪拌する攪拌手段を有することを特徴とする第1～6の手段のいずれかに記載の光触媒を用いた水処理装置である。

【0022】第8の手段は、前記紫外線を含有する光とは、太陽光、蛍光灯、ブラックライト、殺菌灯、水銀灯、ハロゲンランプ及び白熱ランプの光より成る群から

選ばれる少なくとも一種の光であることを特徴とする第1～7の手段のいずれかに記載の光触媒を用いた水処理装置である。

【0023】第9の手段は、前記被処理水とは、生活排水、下水処理場排水、廃棄物処理施設排水、紙パルプ製造施設排水、アルミニウム製品製造工場排水、塩化ビニル製造工場排水、農業排水、ゴルフ場排水、着色排水より成る群から選ばれる少なくとも一種であることを特徴とする第1～8の手段のいずれかに記載の光触媒を用いた水処理装置である。

【0024】第10の手段は、前記被処理水中の有機物濃度により、前記光触媒を用いた水処理装置への、前記被処理水の流入排出を制御する制御手段を有することを特徴とする第1～9の手段のいずれかに記載の光触媒を用いた水処理装置である。

【0025】第11の手段は、被処理水中の有機物を分解する水処理装置であって、光触媒を担持した繊維集合体と、紫外線を含有する光を照射する光照射手段とを備え、前記被処理水に浸漬された前記光触媒を担持した繊維集合体へ、前記光照射手段により光を照射することで、前記被処理水中の有機物を分解することを特徴とする光触媒を用いた水処理装置である。

【0026】第12の手段は、前記光触媒を担持した繊維集合体が、光触媒を担持したアルミニウム繊維であることを特徴とする第11の手段に記載の光触媒を用いた水処理装置である。

【0027】第13の手段は、被処理水中の有機物を分解する水処理装置であって、多数の繊維状物にて形成されているシート状布であって、前記各繊維の表面には光触媒が担持され、且つ、その各繊維は、外部より照射される光が前記光触媒へ到達できるように配置されたものであり、且つ、その各繊維は、前記被処理水が処理目的に応じた通過量で通過できるように、互いの位置関係が配置されたものであるシート状布と、前記光触媒へ光を照射する光源とを有し、前記被処理水を前記光が照射されているシート状布を通過させる際に、前記被処理水中の前記有機物を分解させることを特徴とする水処理装置である。

【0028】

【発明の実施の形態】以下、図を参照しながら本発明の実施の形態について説明する。図1は本発明の実施の形態にかかる、光触媒を用いた上下往復運動型水処理装置（以下、往復型装置と記載する。）の縦断面図であり、図2は本発明の異なる実施の形態にかかる、検出器の付いた光触媒を用いた上下往復運動型水処理装置（以下、検出器付き往復型装置と記載する。）の縦断面図であり、図3は本発明の異なる実施の形態にかかる、検出器の付いた光触媒を用いた攪拌型水処理装置（以下、検出器付き攪拌型装置と記載する。）の縦断面図であり、図4は検出器付き攪拌型装置の横断面図であり、図5は本

発明の異なる実施の形態にかかる、光触媒を用いた連続型水処理装置（以下、連続型装置と記載する。）の縦断面図である。尚、各図面の対応する部分には同様の符号を付して示した。

【0029】以下、本発明の実施の形態例を図面に基づき説明する。図1に示す往復型装置において、水槽1内には、後述する光触媒担持網状シート4と、ブラックライト6を入れたガラス管5と、を固定している籠枠9が設置される。さらに籠枠9全体は、中心棒3を介して円盤付きモーター2の円盤に連結され、円盤付きモーター2の回転により上下往復運動する。一方、水槽1には被処理水の取入口11と処理後の水の排出口12が設けられており、各々電動ボールバルブ7、8が設置されている。

【0030】ここで、光触媒担持網状シート4として以下のようなものが好ましく使用できる。例えば、網状のガラス繊維布をシリコン樹脂のエマルジョンに浸漬して引き上げ290℃で加熱して、ガラス繊維布の表面にシリコン樹脂層を形成させ、ポリテトラフルオロエチレン樹脂（PTFE）粉末のディスパージョンをシリコン樹脂上に塗布し、370℃で加熱してPTFE層を形成し、その後ガラスビーズを含むPTFE粉末のディスパージョンをPTFE層上に塗布し、370℃で加熱してガラスビーズを含むPTFE層を形成し、次にPTFE粉末及びアナターゼ型光触媒酸化チタン微粒子を含むディスパージョンを、ガラスビーズを含むPTFE層上に塗布し、370℃で加熱して、表面に付着量20～45.0g/m²の光触媒酸化チタン微粒子（平均粒子径は0.007～0.5μmの範囲、石原産業社製の商品名ST-41、このST-41の電子顕微鏡による粒径は0.2μmである）を含むPTFE層を形成させたシート布状の膜構造材である。上述のような処理をおこなうことで、各繊維の表面には光触媒が担持され、且つ、その各繊維は、外部より照射される光が前記光触媒へ到達できるように配置されたものとなる。市販品としては、日東電工製、ファインキープPFG-SW20H等が好ましく使用できる。

【0031】光触媒担持網状シート4の異なる好ましい例として、網状の耐水性の光触媒紙を用いてもよい。また、光触媒とヤシ殻活性炭や合成ゼオライトなどの吸着剤とを複合化して繊維基材中に光触媒を担持させた耐水性の紙で、二次加工して柔軟性を持たせ、表面積を増やした光触媒クレープも好ましい。さらに、波形状の光触媒シートと平らな光触媒シートを順次積層して接着し、単位体積当たりのシート表面積を増した光触媒コルゲートを使用するのも好ましい。

【0032】さらに加えて、光触媒担持網状シートのかわりに、光触媒を担持させた繊維を集合した光触媒繊維集合体を用いるのも好ましい構成である。この繊維集合体はこれら各繊維に被処理水及び光が到達するように

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集合してあれば、どのような形状でもよい。上記光触媒担持網状シートと同様のシート状に形成すれば、光触媒担持網状シートと同様の作用をすることができる。被処理水が接触し易い繊維としては、アルミニウム繊維、ガラス繊維、炭素繊維等がある。これら繊維の表面に光触媒を担持させた後に糸状にしたり、スポンジ状にしたり、あるいは、これら繊維を糸状やスポンジ状にした後に表面へ光触媒を担持させたものを用いるのも好ましい。籠枠9への光触媒担持網状シート4の設置量は、被処理水の時間当たりの処理量、分解すべき有機物の種類、含有量、等の条件により適宜設定すればよい。

【0033】次に、ブラックライト6は外側をガラス管5等で保護した上で、籠枠9に設置する。ブラックライト6の本数およびワット数も被処理水の時間当たりの処理量、分解すべき有機物の種類、等の条件により適宜設定すればよい。ここで、光触媒へ光を与える光源としては、ブラックライト6に加えて太陽光、蛍光灯、殺菌灯、水銀灯、ハロゲンランプ、白熱ランプ、等を単独で、または組み合わせて用いることができる。光源として何を用いるかは、本水处理装置が設置される場所のユーティリティ等により適宜、選択すればよい。尚、本実施の形態の説明においては、光源としてブラックライト6を用いたものを例として説明する。

【0034】上述のようにして、光触媒担持網状シート4とブラックライト6とが設置された籠枠9は円盤付きモーター2により被処理水中で、上下往復運動をおこなう。ここで、光触媒担持網状シート4が網状であるため、単位時間に光触媒担持網状シート4表面に接触する被処理水の量を飛躍的に多くして分解効率を向上させることができる。さらに網状であるため水の抵抗が少なく、少ないエネルギーで、被処理水との接触効率を飛躍的に上げることもできた。

【0035】この結果、被処理水中に浸漬される光触媒担持網状シート4と、紫外線を含有する光を当該シートに照射する手段とを有することにより、単位時間に光触媒表面に接触する水の量を多くし、光触媒担持網状シート4表面へ紫外線照射することにより生成したヒドロキシラジカルが、接触した被処理水中の有機物である、例えば、有機塩素系化合物や内分泌攪乱化学物質、農薬、有機着色物質、等を高速度で分解することが可能になったものである。さらにこの構成を採ることにより、光触媒担持網状シート4は被処理水中で光の照射を受けることとなり、たとえ有機物が光触媒担持網状シート4に吸着され難いものであったとしても、光触媒担持網状シート4上で生成したヒドロキシラジカルにより分解されるものである。

【0036】図2に示す検出器付き往復型装置は、図1に示した往復型装置へフローセル10と検出器21とを設けたものである。この構成を採ることにより、検出器21を介して、検出器21の測定値により自動的に流入

用電動ボールバルブ7と排出用電動ボールバルブ8の開閉を制御することが可能となる。水槽1から極微量の被処理水をフローセル10に通し、有機物濃度を検出する検出器21で、有機物の分解程度を測定し、この分解程度により、水槽1への流入及び排出の電動ボールバルブ7、8を自動的に制御する装置を取り付けると、被処理水の有機物量に変動がある場合においても、水槽1より排出される被処理水の有機物濃度を一定以下に抑えることが可能となり好ましい。

【0037】フローセル10の検出部には、例えば、高感度のダイヤモンド電極（導電性シリコン基板上にマイクロ波プラズマCVD装置によりホウ素ドーパの導電性ダイヤモンド多結晶薄膜を成膜したもの）を作用電極と、白金電極を対極と、銀塩化銀電極を参照極と、する。検出器21にはリニアスweepボルタメトリーを使用することにより、フローセル10に配置したダイヤモンド電極と白金電極の間の有機物濃度に依存する電流を検出することができる。

【0038】図3に示す検出器付き攪拌型装置は、図1、2に示した籠枠9の代わりに円筒籠枠20を用い、これをモーター23を用いて水槽22中で回転させるものの例である。図4はこの検出器付き攪拌型装置の横断面図である。この例においては水槽22の内壁に、ブラックライト6を入れたガラス管5と、光触媒担持網状シート4を固定し、さらに、光触媒担持網状シート4を円筒籠枠20へ放射状に固定したものである。円筒籠枠20の中心棒3はモーター23に連結され、回転する。尚、この回転を、正回転と逆回転の組み合わせとするのも好ましい構成である。

【0039】この構成を採ることにより、光触媒担持網状シート4の回転運動により、単位時間に光触媒表面に接触する被処理水の量を多くすることが可能になった。光触媒担持網状シート4は網状であるために、被処理水中で回転させても、水の抵抗が少なく、回転に必要なエネルギーは少なくて済む。また、光触媒網状シート4を所定時間ごとに反転させることにより、一方向に回転させる場合に比して、さらに光触媒を被処理水に接触させる効率をあげることも可能であり好ましい。

【0040】さらに、設置場所の要請等により、図3に示す検出器付き攪拌型装置を転倒させた形の構成を採ることもできる。その場合、回転軸3は水平に回転する。

【0041】さらに加えて、単位時間に光触媒担持網状シート4表面に接触する被処理水の量をさらに多くする手段として、光触媒担持網状シート4を運動させる方法に加え、水槽1、22の底部等にスクレーパー等を取り付け、これを回転させて水を攪拌するのも好ましい構成である。

【0042】図5に示す連続型装置は、筒型塔24を仕切板25により5部屋に区切り、各部屋にはブラックライト6を入れたガラス管5を設け、そこへ光触媒担持網

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状シート4を並べたものである。筒型塔24には、被処理水を流入させ、滞留時間を調節するために、取入口11に流入量調整バルブ26と、排出口12に排出量調整バルブ27とが配置されている。筒型塔24に仕切板25を設けることで被処理水の流路を長くした。このことにより光触媒担持網状シート4単位断面積当たりの被処理水の流速を早めることを可能にし、有機物の分解速度を向上させたものである。この構成においては、さらに被処理水の流速を利用して、光触媒担持網状シート4を往復、振動、旋回運動させることで、光触媒に接する被処理水量をさらに増加させることもでき好ましい。

【0043】以上、詳述した本発明の実施の形態にかかる光触媒を用いた水処理装置を一般廃棄物焼却施設や産業廃棄物焼却施設や紙パルプ製造施設排水、アルミニウム製品製造工場排水、塩化ビニル製造工場排水の排水処理の最終段階に設置すれば、ダイオキシン類の排出基準の 10 pg-TEQ/L 以下の濃度にまで下げることが容易にできる。また下水処理場の最終処理の段階に、この水処理装置を設置すれば、 17β -エストラジオールやエチニルエストラジオールの除去率も格段に向上し、河川中の 17β -エストラジオールやエチニルエストラジオールの濃度が減少し、河川に棲息する鯉の異常を改善することができる。さらに、この水処理装置を農業やゴルフ場の排水施設に設置すれば、内分泌攪乱化学作用を有すると疑われている農薬（2,4-ジクロロフェノキシ酢酸（2,4-PA）、アトラジン、シマジン（CAT）、カルバリル（NAC）、メソミル、ベノミル、馬拉チオン（馬拉松）、アラクロール、トリフルラリン）を、公共用水域等における水質評価指針やゴルフ場使用農薬に係る暫定指導指針以下の濃度に下げることができる。さらに加えて、この水処理装置を着色インクや染料の有機着色成分を含む排水施設に設置すれば、排水の脱色も容易にできるものである。

【0044】（実施例1）図1に示した往復型装置を用いた。水槽1として、縦950mm、横950mm、高さ1400mmの角形水槽を使用した。光触媒担持網状シート4として「日東電工製、ファインキープPFG-SW20H、厚さ0.30mm、糸幅0.5mm、目あき幅1mm、格子状、開孔率49%、光触媒酸化チタン微粒子表面への付着量 115 g/m^2 」を用い、籠枠（縦900mm、横900mm、高さ1000mm）9に、100枚（幅900mm長さ900mmの広さ）を10mm間隔に水平に固定した。次に、長さ1198mmの40Wブラックライト6を入れたガラス管5を、16本等間隔で鉛直に籠枠9に固定した。

【0045】そして、水槽1の排出用電動ボールバルブ8を閉じ、流入用電動ボールバルブ7を開け、ダイオキシン類のモデル物質として2,4-ジクロロフェノール $90\text{ }\mu\text{g/L}$ （ $5.5 \times 10^{-7}\text{ mol/L}$ ）を含んだ 0.90 m^3 の水を深さ1000mmまで入れた。ここで1

6本のブラックライト6を点灯し、単相、100V、200Wの円盤付きモーター2を60rpmの速さで中心棒3により籠枠9全体を40mm上下運動させた。すると運転開始後15分間で2,4-ジクロロフェノールは $9.0\text{ }\mu\text{g/L}$ （初期濃度の10分の1）になり、30分間で $0.90\text{ }\mu\text{g/L}$ （初期濃度の100分の1）になった。そこで、初期濃度の100分の1になった30分後に、排出用電動ボールバルブ8を開け、水槽1の被処理水を排出した。排出用電動ボールバルブ8を閉めた後、流入用電動ボールバルブ7を開け、再び処理すべき水を深さ900mmまで入れ装置を運転した。このサイクルで本装置を1日運転すると 43 m^3 の被処理水の有機物を初期濃度の100分の1以下に処理することができた。

【0046】（実施例2）被処理水中の分解すべき有機物として2,4-ジクロロフェノール $90\text{ }\mu\text{g/L}$ （ $5.5 \times 10^{-7}\text{ mol/L}$ ）を 17β -エストラジオール $90\text{ }\mu\text{g/L}$ （ $3.3 \times 10^{-7}\text{ mol/L}$ ）へ換えた以外は、実施例1と同様の条件で本装置を運転した。すると、 17β -エストラジオールは6分間で $9.0\text{ }\mu\text{g/L}$ （初期濃度の10分の1）に、12分間で $0.90\text{ }\mu\text{g/L}$ （初期濃度の100分の1）になった。

【0047】（実施例3）被処理水中の分解すべき有機物として2,4-ジクロロフェノール $90\text{ }\mu\text{g/L}$ （ $5.5 \times 10^{-7}\text{ mol/L}$ ）を水田用除草剤である2,4-ジクロロフェノキシ酢酸（2,4-PA）のナトリウム塩 1.0 mg/L （ $4.5 \times 10^{-6}\text{ mol/L}$ ）へ換えた以外は、実施例1と同様の条件で本装置を運転した。すると、2,4-ジクロロフェノキシ酢酸は10分間で 0.10 mg/L （初期濃度の10分の1）に、20分間で 0.010 mg/L （初期濃度の100分の1）になった。

【0048】（実施例4）被処理水中の分解すべき有機物として2,4-ジクロロフェノール $90\text{ }\mu\text{g/L}$ （ $5.5 \times 10^{-7}\text{ mol/L}$ ）を着色染料メチレンブルー水溶液 10 mg/L へ換えた以外は、実施例1と同様の条件で本装置を運転した。すると、メチレンブルーは15分間で 1.0 mg/L （初期濃度の10分の1）に、30分間で 0.10 mg/L （初期濃度の100分の1）になり、溶液が透明になった。

【0049】（実施例5）被処理水中の分解すべき有機物として2,4-ジクロロフェノール $90\text{ }\mu\text{g/L}$ （ $5.5 \times 10^{-7}\text{ mol/L}$ ）を、着色染料エオシンY水溶液 20 mg/L に換えた以外は、実施例1と同様の条件で本装置を運転した。すると、エオシンYは15分間で 2.0 mg/L （初期濃度の10分の1）に、30分間で 0.20 mg/L （初期濃度の100分の1）になり、溶液が透明になった。

【0050】（実施例6）図2に示した検出器付き往復型装置を用いた、これは実施例1の装置にフローセル1

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0と検出器21を設置したものである。フローセル10内部には、高感度のダイヤモンド電極（導電性シリコン基板上にマイクロ波プラズマCVD装置によりホウ素ドーパの導電性ダイヤモンド多結晶薄膜を成膜したもの）を作用極、白金電極を対極、銀・塩化銀電極を参照極として配置した。検出器21としてリニアスイープボルタンメトリーを用いた。被処理水中の分解すべき有機物としてビスフェノールA $90 \mu\text{g/L}$ ($3.9 \times 10^{-7} \text{mol/L}$)を用いた。

【0051】まず水槽1の水を連続的にフローセル10に取り込み、pH7.2のリン酸緩衝液を支持電解質として加えた。フローセル10の流速を 1mL/min とし、高感度のダイヤモンド電極の電位を $+0.75 \text{V}$ にして電流値を測定すると 4.0nA を示した。実施例1と同様に光触媒担持網状シート4を上下往復運動し、ブラックライト6の光を照射して、10分間を運転すると、電位 $+0.75 \text{V}$ で電流値 0.40nA を示し、ビスフェノールAは初期濃度の10分の1の $9.0 \mu\text{g/L}$ になったことがわかった。光触媒担持網状シート4を上下往復運動し、ブラックライト6の光を照射して、装

置を20分間運転すると、電位 $+0.75 \text{V}$ で電流値 0.04nA を示し、ビスフェノールAは初期濃度の100分の1の $0.9 \mu\text{g/L}$ になったことが判明した。

【0052】（実施例7）被処理水中の分解すべき有機物としてビスフェノールA $90 \mu\text{g/L}$ ($3.9 \times 10^{-7} \text{mol/L}$)を、農薬であるカルバリル (NAC) 1.0mg/L ($5.0 \times 10^{-6} \text{mol/L}$)に換えた以外は、実施例6と同様にして処理装置を運転した。水槽1の水を連続的にフローセル10に取り込み、pH7.2のリン酸緩衝液を支持電解質として加えた。フローセル10の流速を 1mL/min とし、高感度のダイヤモンド電極の電位を $+1.4 \text{V}$ にして電流値を測定すると 100nA を示した。光触媒担持網状シート4を上下往復運動し、ブラックライト6の光を照射して、10分間を運転すると、電位 $+1.4 \text{V}$ で電流値 10nA を示し、カルバリルは初期濃度の10分の1の 0.1mg/L になったことがわかった。光触媒担持網状シート4を上下往復運動し、ブラックライト6の光を照射して、20分間を運転すると、電位 $+1.4 \text{V}$ で電流値 1.0nA を示し、カルバリルは初期濃度の100分の1の 0.01mg/L になったことが判明した。

【0053】（実施例8）図3に示した検出器付き攪拌型装置を使用した。直径 900mm 、高さ 1050mm の円筒型の水槽22に、長さ 1198mm の 40W ブラックライト6を入れたガラス管5を水槽の内壁に、8本等間隔に固定した。光触媒担持網状シート4として「日東電工製、ファインキープPFG-SW20H、厚さ 0.30mm 、糸幅 0.5mm 、目あき幅 1mm 、格子状、開孔率 49% 、光触媒酸化チタン微粒子表面への付着量 115g/m^2 」を用い、幅 320mm 長さ 1m の

広さの光触媒担持網状シート4を32枚、中心棒3の周囲に放射状に出た長さ 320mm の円筒籠枠20に取り付けた、この横断面を図4に示す。さらに図4に示すように水槽22の内壁に、幅 6mm 長さ 1m の広さの光触媒担持網状シート4を32枚等間隔に固定した。

【0054】そして水槽22の排出用電動ボールバルブ8を閉じ、流入用電動ボールバルブ7を開け、被処理水中の分解すべき有機物としてビスフェノールA $90 \mu\text{g/L}$ ($3.9 \times 10^{-7} \text{mol/L}$)を含んだ 0.56m^3 の被処理水を深さ 900mm まで入れた。ここで、8本のブラックライト6を点灯し、単相、 100V 、 200W モーター23で中心棒3を 60rpm の速さで15秒間回転させ、5秒間休止させ、15秒間反転させ、5秒間休止させた。この操作を繰り返し行い、被処理水を攪拌した。

【0055】一方、高感度のダイヤモンド電極（導電性シリコン基板上にマイクロ波プラズマCVD装置によりホウ素ドーパの導電性ダイヤモンド多結晶薄膜を成膜したもの）を作用極、白金電極を対極、銀塩化銀電極を参照極として内部に配置したフローセル10に、円筒水槽22の水を連続的に、流速を 1mL/min で取り込み、pH7.2のリン酸緩衝液を支持電解質として加えた。検出器21のリニアスイープボルタンメトリーの電位を $+0.75 \text{V}$ にして電流値を測定すると 4.0nA を示した。そこで、光触媒担持網状シート4を反転し、水を攪拌しながらブラックライト6の光を照射して、20分間を運転すると、電位 $+0.75 \text{V}$ で電流値 0.40nA を示し、ビスフェノールAは初期濃度の10分の1の $9.0 \mu\text{g/L}$ になったことが判明した。

【0056】さらに、攪拌しながらブラックライト6の光を照射して装置を40分間運転すると、電位 $+0.75 \text{V}$ で電流値 0.04nA を示し、ビスフェノールAは初期濃度の100分の1である $0.9 \mu\text{g/L}$ になったことが判明した。そして初期濃度の100分の1になった運転開始40分後に、排出用電動ボールバルブ8を開け、円筒水槽22の処理水を排出した。次に、排出用電動ボールバルブ8を閉めた後、流入用電動ボールバルブ7を開け、再び処理すべき水を深さ 900mm まで入れ、装置を運転した。このサイクルで本装置を1日運転すると 20m^3 の被処理水の有機物を初期濃度の100分の1以下に処理することができた。

【0057】（実施例9）図5に示した連続型装置を用いた。筒型塔24（高さ 2.5m で内径 $0.95 \text{m} \times 0.95 \text{m}$ ）の内部に 0.5m 間隔に $0.95 \text{m} \times 0.90 \text{m}$ で厚さ 4mm の仕切板25を図5に示すように4枚取り付け、5部屋に区切り、流路を 5.4m とした。

長さ 1198mm の 40W ブラックライト6を入れたガラス管をお互いに 0.5m 離し、各部屋に2本ずつ、合計10本取り付け付けた。各部屋には、光触媒担持網状シート4「日東電工製、ファインキープPFG-SW20

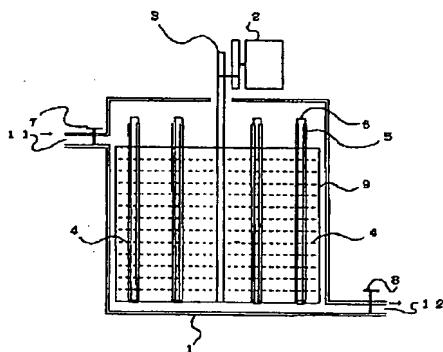
H、厚さ0.30mm、糸幅0.5mm、目あき幅1mm、格子状、開孔率49%、光触媒酸化チタン微粒子表面への付着量 115 g/m^2 を $0.95\text{ m} \times 0.42\text{ m}$ のサイズとしたもの90枚を10mm間隔に垂直に並べた。

【0058】被処理水中の分解すべき有機物として 17β -エストラジオール $90\text{ }\mu\text{g/L}$ ($3.3 \times 10^{-7}\text{ mol/L}$)を含んだ被処理水を、流速 $0.038\text{ m}^3/\text{min}$ となるように流入量調整バルブ26を調整し、筒型塔24に連続的に流入させ、滞留時間が80分間となるように排出量調整バルブ27を調整し、ブラックライト6を点灯した。すると、筒型塔9より流出する被処理水中の 17β -エストラジオールは $0.90\text{ }\mu\text{g/L}$ (初期濃度の100分の1)になった。この流速で本装置を1日運転すると 55 m^3 の被処理水中の 17β -エストラジオールを流入濃度の100分の1以下に処理できることが判明した。

【0059】

【発明の効果】以上詳述したように、本発明においては、被処理水中の有機物を分解する水処理装置であって、光触媒を担持した網状シートと、紫外線を含有する光を照射する光照射手段とを備え、前記被処理水に浸漬された前記光触媒を担持した網状シートへ、前記光照射手段により光を照射することで、前記被処理水中の有機物を分解することを特徴とする光触媒を用いた水処理装*

【図1】



* 置を発明した。この水処理装置を用いることで、エネルギーをあまり必要とせず水処理費用を低く抑える一方、被処理水と光触媒との接触の効率を上げることにより、被処理水中における有機物の分解を早い速度でおこなうことが可能となった。

【図面の簡単な説明】

【図1】本発明の実施の形態にかかる往復型装置の縦断面図である。

【図2】本発明の実施の形態にかかる検出器付き往復型装置の縦断面図である。

【図3】本発明の実施の形態にかかる検出器付き攪拌型装置の縦断面図である。

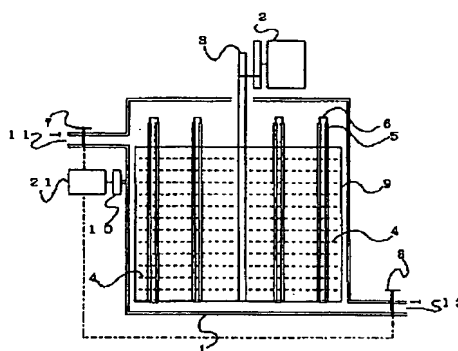
【図4】本発明の実施の形態にかかる検出器付き攪拌型装置の横断面図である。

【図5】本発明の実施の形態にかかる連続型装置の縦断面図である。

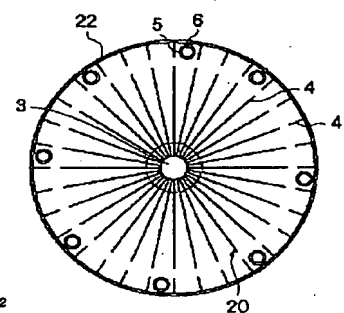
【符号の説明】

1. 水槽、2. 円盤付きモーター、3. 中心棒、4. 光触媒担持網状シート、5. ガラス管、6. ブラックライト、7. 流入用電動ボールバルブ、8. 排出用電動ボールバルブ、9. 籠枠、10. フローセル、11. 取入口、12. 排出口、20. 円筒籠枠、21. 検出器、22. 水槽、23. モーター、24. 筒型塔、25. 仕切板、26. 流入量調整バルブ、27. 排出量調整バルブ。

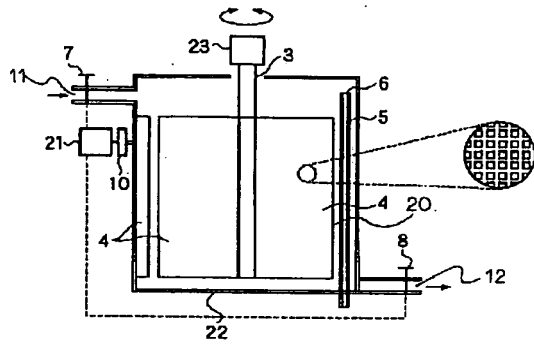
【図2】



【図4】



【図3】



【図5】

